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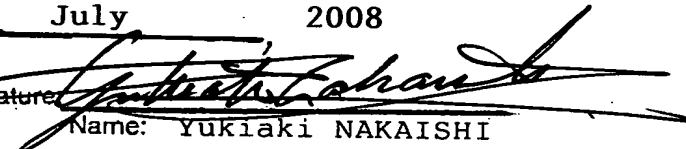
Title: OXYNITRIDE FLUORESCENT MATERIAL AND LIGHT-EMITTING DEVICE

ACCURATE TRANSLATION OF PRIORITY DOCUMENT

The undersigned, of the below address, hereby states that he/she well knows both the English and Japanese languages, and that the attached is an accurate translation into the English language of the Certified Copy, filed for this application under 35 U.S.C. Section 119 and/or 365, of:

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[SUBMITTED DOCUMENTS]

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**【NAME OF DOCUMENT】 SCOPE OF PATENT CLAIMS**

**【Claim 1】**

An oxynitride fluorescent material, which contains  
as a main component a crystal phase represented by a  
5 general formula  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$ , with an optically active  
element (M) added thereto as a luminescence center.

**【Claim 2】**

The oxynitride fluorescent material according to  
claim 1, where said optically active element (M) comprises  
10 one or two or more elements selected from Mn, Ce, Pr, Nd,  
Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

**【Claim 3】**

An oxynitride fluorescent material, which contains  
as a main component a crystal phase represented by a  
15 general formula  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$ , where  $0 < x \leq 4$ , with an  
optically active element (M) added thereto as a  
luminescence center.

**【Claim 4】**

The oxynitride fluorescent material according to  
20 claim 3, wherein said optically active element (M)  
comprises one or two or more elements selected from Mn, Ce,  
Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

**【Claim 5】**

The oxynitride fluorescent material according to  
25 claim 4, wherein x is  $0 < x \leq 2$ .

**【Claim 6】**

The oxynitride fluorescent material according to any  
one of claims 1 to 5, wherein at least Ce is contained as  
said optically active element (M).

30 **【Claim 7】**

The oxynitride fluorescent material according to any

one of claims 1 to 6, wherein at least Tb is contained.

**【Claim 8】**

An oxynitride fluorescent material, which comprises an optically active element (M) and elements La, Si, Al, N  
5 and O, where M is one or two or more elements selected from Mn, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, has a compositional formula  $M_aLa_bSi_cAl_dN_eO_f$  provided that  $a+b=3$ , and satisfies all conditions (i), (ii), (iii), (iv) and (v):

- 10             $0.00001 \leq a \leq 2.5$             (i)  
              $4 \leq c \leq 10$                     (ii)  
              $0 \leq d \leq 4$                       (iii)  
              $7 \leq e \leq 14$                     (iv)  
              $2 \leq f \leq 8$                       (v)

15    **【Claim 9】**

The oxynitride fluorescent material according to claim 8, wherein  $d=0$ .

**【Claim 10】**

20    The oxynitride fluorescent material according to claim 8 or 9, wherein  $c=8$ ,  $e=11$ , and  $f=4$ .

**【Claim 11】**

The oxynitride fluorescent material according to any one of claims 8 to 10, wherein Ce is selected as an M component.

25    **【Claim 12】**

The oxynitride fluorescent material according to any one of claims 8 to 10, wherein Tb is selected as said optically active element (M).

**【Claim 13】**

30    The oxynitride fluorescent material according to any one of claims 1 to 12, which comprises a mixture of a

$\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  crystal phase where  $0 < x \leq 4$  with other crystal phase or an amorphous phase, and having a  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  crystal phase content of at least 50% by mass.

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【NAME OF DOCUMENT】 SPECIFICATION

【TITLE OF THE INVENTION】

OXYNITRIDE FLUORESCENT MATERIAL

【TECHNICAL FIELDS】

5 【0001】

The present invention relates generally to a silicon oxynitride fluorescent material composed primarily of a crystal phase represented by general formula  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  where  $0 < x \leq 4$ .

10 【BACKGROUND TECHNOLOGY】

【0002】

Fluorescent materials are used for vacuum fluorescent display tubes (VFDs), field emission displays (FEDs), plasma display panels (PDPs), cathode-ray tubes (CRTs), white light-emitting diodes (LEDs), etc. To allow the fluorescent material to emit light in any application, energy for exciting it must be supplied to it. Upon excitation by an excitation source having high energy such as vacuum ultraviolet radiation, ultraviolet radiation, electron radiation, blue light or the like, the fluorescent material gives out visible light rays. A problem with the fluorescent material is, therefore, that its luminance drops as a result of exposure to such an excitation source as mentioned above. To overcome that problem, sialon fluorescent materials have been proposed as those having more limited luminance decreases than do prior art fluorescent materials based on silicates, phosphates, aluminates, and sulfides.

【0003】

30 The sialon fluorescent material, for instance, has been prepared by mixing together silicon nitride ( $\text{Si}_3\text{N}_4$ ),

aluminum nitride (AlN) and europium oxide (Eu<sub>2</sub>O<sub>3</sub>) at a given molar ratio, and then subjecting the resulting mixture to hot-press firing wherein it is held at a temperature of 1,700°C for 1 hour in nitrogen of 1 atm  
5 (0.1 MPa) (for instance, see patent publication 1).  $\alpha$ -sialon with activated Eu ions, obtained by this method, has been reported to provide a fluorescent material that is excited by blue light of 450 to 500 nm, giving out yellow light of 550 to 600 nm. For applications such as  
10 white LEDs or plasma displays using an ultraviolet LED as an excitation source, however, fluorescent materials emitting not only yellow light but also blue light of 420 nm to 470 nm or green light of 500 nm to 550 nm are also still in need.

15           【Patent Publication 1】 JP(A)2002-363554

          【DISCLOSURE OF THE INVENTION】

          【PROBLEMS TO BE SOLVED BY THE INVENTION】

          【0004】

          The primary object of the invention is to provide an  
20 oxynitride fluorescent material capable of emitting light having a far wider range of wavelengths than could be achievable with conventional rare earth-activated sialon fluorescent materials.

          【0005】

25           Such being the case, we have made study after study about fluorescent materials that contain an optically active element M and elements La, Si, Al, N and O, where M is one or two or more elements selected from Mn, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, and  
30 consequently found out that a material having a specific composition domain range and a specific crystal phase can

provide a fluorescent material that emits blue light of about 450 nm and green light of about 540 nm. That is, we have found out that a crystal comprising a  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  where  $0 < x \leq 4$  with M (one or two or more elements selected from Mn, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) added thereto as a luminescence center can provide a florescent material capable of emitting blue or green light.

【0006】

10 The  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  crystal phase, occurring by high-temperature firing of a composition approximate to  $\text{La}_2\text{O}_3\text{-}2\text{Si}_3\text{N}_4$ , has been synthesized by M. Mitomo et al. and indexed by X-ray diffraction, and before the filing of this application, its details have already been reported  
15 at great length in academic literature (see non-patent publication 1).

【0007】

After that, R. K. Harris et al. identified the exact composition of that crystal to be  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  and reported  
20 its details at great length in academic literature (non-patent publication 2).

【0008】

The  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  crystal phase is a solid solution made up of a  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  crystal containing Al and  
25 O. Details of that crystal phase, synthesized and structurally analyzed by Jekabs Grins et al., were reported at great length in academic literature (see non-patent publication 3), too, before filing of this application.

30 【Non-Patent Publication 1】

M. Mitomo and three others, "Journal of Materials Science",

1982, Vol. 17, pp. 2359-2364

【Non-Patent Publication 2】

R. K. Harris and two others, "Chemical Materials", 1992, Vol. 4, pp. 260-267

5       【Non-Patent Publication 3】

Jekabs Grins and three others, "Journal of Materials Chemistry", 2001, Vol. 11, pp. 2358-2362

      In any case, as far as the process of research of the sintering of silicon nitride has gone, the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  crystal phase per se has been  
10 exclusively studied for their heat resistance; never until now is there any study about using them as a fluorescent material. That the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  crystal phase can be used as a fluorescent material that is  
15 excited by ultraviolet radiation, visible light, and electron radiation, giving out red light with high luminance, has been discovered by us for the first time. We have extended this finding to further research, resulting in a discovery of a unique light emission  
20 phenomenon having improved luminance properties in a specific wavelength range, as embodied in (1) to (13) below. Having been made as a result of a series of researches on the basis of the aforesaid findings, the present invention successfully provides an oxynitride  
25 fluorescent material capable of emitting light with ever higher luminance, and a lighting device using the same.

(1) An oxynitride fluorescent material, characterized by containing as a main component a crystal phase represented by a general formula  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$ , with an  
30 optically active element (M) added thereto as a luminescence center.

(2) The oxynitride fluorescent material according

to (1) above, characterized in that said optically active element (M) comprises one or two or more elements selected from Mn, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

5           (3)    An oxynitride fluorescent material, characterized by containing as a main component a crystal phase represented by a general formula  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$ , where  $0 < x \leq 4$ , with an optically active element (M) added thereto as a luminescence center.

10           (4)    The oxynitride fluorescent material according to (3) above, characterized in that said optically active element (M) comprises one or two or more elements selected from Mn, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

15           (5)    The oxynitride fluorescent material according to (4) above, characterized in that  $x$  is  $0 < x \leq 2$ .

            (6)    The oxynitride fluorescent material according to any one of (1) to (5) above, characterized in that at least Ce is contained as said optically active element (M).

20           (7)    The oxynitride fluorescent material according to any one of (1) to (6) above, characterized in that at least Tb is contained.

            (8)    An oxynitride fluorescent material, characterized by comprising an optically active element  
25   (M) and elements La, Si, Al, N and O, where M is one or two or more elements selected from Mn, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, having a compositional formula  $\text{M}_a\text{La}_b\text{Si}_c\text{Al}_d\text{N}_e\text{O}_f$  provided that  $a+b=3$ , and satisfying all conditions (i), (ii), (iii), (iv) and (v):

- 30            $0.00001 \leq a \leq 2.5$                    (i)  
             $4 \leq c \leq 10$                        (ii)  
             $0 \leq d \leq 4$                        (iii)

$$7 \leq e \leq 14 \quad (\text{iv})$$

$$2 \leq f \leq 8 \quad (\text{v})$$

(9) The oxynitride fluorescent material according to (8) above, characterized in that  $d=0$ .

5 (10) The oxynitride fluorescent material according to (8) or (9) above, characterized in that the values of  $c$ ,  $e$  and  $f$  are  $c=8$ ,  $e=11$  and  $f=4$ , respectively.

(11) The oxynitride fluorescent material according to any one of (8) to (10) above, characterized in that Ce is selected as an M component.

(12) The oxynitride fluorescent material according to any one of (8) to (10) above, characterized in that Tb is selected as said optically active element (M).

15 (13) The oxynitride fluorescent material according to any one of (1) to (12) above, characterized by comprising a mixture of a  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  crystal phase where  $0 < x \leq 4$  with other crystal phase or an amorphous phase, and having a  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  crystal phase content of at least 50% by mass.

## 20 **【ADVANTAGES OF THE INVENTION】**

### **【0009】**

The oxynitride fluorescent material provided by the invention with the aforesaid unique structure is comprised of the basic or matrix crystal and the optically active  
25 element M. Only with the basic crystal (called the matrix crystal) free of M, however, there is no light emission. In other words, with either a structure wherein a part of components of the basic crystal phase represented by  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  where  $0 < x \leq 4$  is substituted  
30 by the optically active element (M) in a solid solution form or a solid solution structure wherein the optically

active element (M) penetrates through the crystal space of that crystal phase, fluorescent emission capabilities come out. The basic crystal (matrix crystal) (i) absorbs excitation light to transmit energy to M, and (ii) changes an electron state around M to have influences on emission colors or emission intensities. The fluorescent material allows both (i) and (ii) to cooperate to emit light, and the light emission properties are determined and governed by how the matrix crystal combines with the activation element. The fluorescent material has advantages over the prior art sialon fluorescent materials in that higher luminance is obtainable, and upon exposure to excitation sources, the material is lesser susceptible to deteriorate and luminance drops are much more reduced, and so it is well fit for VFDs, FEDs, PDPs, CRTs, white LEDs, etc. Thus, the fluorescent material of the invention provides a novel, useful material for material designs in such fields, and so it would be of great significance and make a lot of contribution to developments of the industry.

20   **【BEST MODE FOR CARRYING OUT THE INVENTION】**

**【0010】**

      The fluorescent material of the invention comprises as its main component a crystal phase having the general formula  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  where  $0 < x \leq 4$ , or a solid solution thereof. In consideration of fluorescence emission, it is here desired that  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  that is the main constituent of the oxynitride fluorescent material be contained as much as possible with high purity, and whenever possible, in a single phase form. Unless there is no property degradation, however, they could be used in admixture with other crystal phase or an amorphous phase.

### 【0011】

Preferably for high luminance, the content of the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  phase should be at least 50% by mass. The term "main component" used herein is understood to mean that the content of the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  phase is at least 50% by mass. Alternatively, a solid solution having the same crystal structure as the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  crystal could be used as the main component. In that solid solution, a part of La is substituted by metals such as Mn, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu; a part of Si is substituted by Al or the like; and a part of N is substituted by oxygen. In the  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  phase, a part of Si is substituted by Al, and a part of N is substituted by O. The range of  $0 < x \leq 4$  wherein x is a parameter indicative of the amount of solid solution ensures that a stable  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  phase occurs. In particular, the range of  $0 < x \leq 2$  ensures that a florescent material having ever higher luminance is obtainable. In addition, simultaneous substitution by two or more elements could be included in the invention.

### 【0012】

With incorporation in a solid solution form of the element M (one or two or more selected from Mn, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) in the matrix of the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  matrix crystal phase, these elements work as luminescence centers, and have fluorescence emission capabilities. Of the elements M, Ce excels in blue light emission capability and Tb excels in green light emission capability.

### 【0013】

In the invention, given the crystal or solid solution of the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  phase, no critical limitation is imposed on the type of composition. With such compositions as specified below, however, a  
5 fluorescent material having ever higher luminance is obtainable because of an increased content of the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  phase.

【0014】

Specific compositions of the invention contain the  
10 elements M, La, Si, Al, N and O where M is one or two or more selected from Mn, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, and have a compositional formula  $\text{M}_a\text{La}_b\text{Si}_c\text{Al}_d\text{N}_e\text{O}_f$  on condition that  $a+b=3$ . The compositional formula stands for the ratio of the number of atoms that  
15 constitutes a given substance, and a substance with a, b, c, d, e and f multiplied by any number has the same composition, too. Consequently, the following conditions are determined for a composition with a, b, c, d, e and f recalculated in such a way as to be  $a+b=3$ .

20 【0015】

In the invention, the values of a, c, d, e and f are selected from the range of values that satisfy all conditions (i), (ii), (iii), (iv) and (v).

$$0.00001 \leq a \leq 2.5 \quad (\text{i})$$

25  $4 \leq c \leq 10 \quad (\text{ii})$

$$0 \leq d \leq 4 \quad (\text{iii})$$

$$7 \leq e \leq 14 \quad (\text{iv})$$

$$2 \leq f \leq 8 \quad (\text{v})$$

【0016】

30 Here, the small letter a stands for the amount of the element added as the luminescence center, and c, d, e

and  $\underline{f}$  represent deviations from the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  composition.

【0017】

The small letter  $\underline{a}$  stands for the amount of the element M added as the luminescence center, which should preferably be determined such that the value of  $3 \times \text{M}/(\text{M}+\text{La})$  that is the ratio of the number of atoms between M and (M+La) in the fluorescent material is in the range of 0.00001 to 2.5 inclusive. As the value of  $3 \times \text{M}/(\text{M}+\text{La})$  is smaller than 0.00001, there is an emission luminance drop because of fewer M's. As the value of  $3 \times \text{M}/(\text{M}+\text{La})$  exceeds 2.5, there is again a luminance drop by reason of concentration quenching responsible ascribable to interferences between M ions.

【0018】

The value of  $\underline{c}$  is the content of Si, given by  $4 \leq c \leq 10$ . For the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  crystal, it is preferable that  $c=8$ , and for the  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  crystal, it is preferable that  $c=8-d$ . As the value of  $\underline{c}$  deviates from this range, there is an emission luminance drop because of no formation of any stable  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  crystal phase.

【0019】

The value of  $\underline{d}$  is the content of Al, given by  $0 \leq d \leq 4$ . For the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  crystal, it is preferable that  $d=0$ , and for the  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  crystal, it is preferable that  $0 < d \leq 2$ . As the value of  $\underline{d}$  deviates from this range, there is an emission luminance drop because of no formation of any stable  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  crystal phase.

【0020】

The value of  $\underline{e}$  is the content of N, given by  $7 \leq e \leq 14$ . For the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  crystal, it is preferable that  $e=11$ ,

and for the  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  crystal, it is preferable that  $e=11-d$ . As the value of  $e$  deviates from this range, there is an emission luminance drop because of no formation of any stable  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  crystal phase.

#### 【0021】

The value of  $f$  is the content of O, given by  $2 \leq f \leq 8$ . For the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  crystal, it is preferable that  $f=4$ , and for the  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  crystal, it is preferable that  $f=4+d$ . As the value of  $f$  deviates from this range, there is an emission luminance drop because of no formation of any stable  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  crystal phase.

#### 【0022】

The fluorescent material of the invention differs in excitation spectra and fluorescent spectra with its composition, and if they are selectively combined, it will provide a variety of emission spectra. In other words, the spectra needed in a particular situation can be determined as desired. In particular, with a composition of the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  phase with Eu added thereto in such a way as to meet  $0.00001 \leq 3 \times \text{Ce}/(\text{Ce}+\text{La}) \leq 2.5$ , higher emission capability is obtainable in a blue range of about 450 nm, and with a composition of the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  phase with Tb added thereto in such a way as to meet  $0.00001 \leq 3 \times \text{Tb}/(\text{Tb}+\text{La}) \leq 2.5$ , higher emission capability is obtainable in a green range of about 540 nm.

#### 【0023】

The crystal phase used herein should preferably be made up of a single  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  phase; however, it could be used in admixture with other crystal phase or an amorphous phase in such a range as not to be

detrimental to emission capability. Preferably for higher luminance, the content of the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  phase should exceed 50% by mass. Thus, the term "main component" means that the content of the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  phase is at least 50% by mass. The proportion of the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  phase to be contained may be found from the ratio of the strongest peaks of the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  or  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  phase and other crystal phase(s) as measured by X-ray diffractometry.

10    **【0024】**

The oxynitride fluorescent material obtained by the fabrication process of the invention is capable of emitting light at a wavelength higher than that at which prior art sialon or oxynitride fluorescent materials are used, and lesser susceptible of luminance degradation upon exposure to excitation sources, and so it lends itself well to VFDs, FEDs, PDPs, CRTs, white LEDs, etc.

**【Examples】**

**【0025】**

20       Although the invention is now explained in further details with reference to specific examples, it is to be understood that they are given as an aid only to a better understanding of the invention, and the invention is never limited thereto.

25    **【0026】**

Example 1;

The starting powders used were silicon nitride powders having an average particle diameter of 0.5  $\mu\text{m}$ , an oxygen content of 0.93% by weight and  $\alpha$ -type content of 92%, lanthanum oxide powders with a 99.9% purity and  
30   cerium oxide powders with a 99.9% purity.

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【0027】

The silicon nitride, lanthanum oxide and cerium oxide powders were weighed in the respective amounts of 46.01% by weight, 43.27% by weight and 10.72% by weight so as to obtain a compound having a compositional formula  $\text{Ce}_{0.57}\text{La}_{2.43}\text{Si}_9\text{N}_{12}\text{O}_{4.5}$  (with mixture compositions of the starting powders shown in Table 1 and compositional parameters shown in Table 2). Then, the powders were mixed together with the addition of hexane in a ball mill for 2 hours, followed by drying in a rotary evaporator. The ensuring compound was molded in a mold with the application of a pressure of 20 MPa to obtain a compact of 12 mm in diameter and 5 mm in thickness.

【0028】

That compact was placed in a boron nitride crucible, which was then set in an electric furnace of the graphite resistance-heating mode. Firing operation was started with evacuation of a firing atmosphere with a diffusion pump. Then, the compact was heated from room temperature up to 800°C at a heating rate of 500°C per hour, and at 800°C nitrogen with a purity of 99.999% by volume was admitted into the furnace to bring the pressure to 1 MPa. Finally, the temperature was brought up to 1,750°C at a rate of 500°C per hour, and at 1,750°C the compact was held for 4 hours. After firing, the constituting crystals of the obtained sintered compact were identified in following manner. As a result, they were judged as a  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  phase. First, the synthesized sample was ground down to powders in an agate mortar for powder X-ray diffraction measurement using  $K_\alpha$  radiation of Cu. The ensuing chart showed a pattern reported in Fig. 1 of non-patent

publication 1, indicative of the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  phase. As a  
result of irradiation of the powder sample with 365-nm  
wavelength light coming from a lamp, it was found to emit  
blue light. As a result of measuring the emission  
5 spectrum and the excitation spectrum of the powder sample  
using a fluorescent emission spectrometer, it was found to  
be a fluorescent material having an excitation spectrum  
peak at 371 nm and a peak at 424-nm blue light in an  
emission spectrum upon excitation by 371-nm ultraviolet  
10 light (Fig. 1). The peak emission intensity was 1,787  
counts. It is here to be noted that the count value  
varies with a measuring device and conditions, so it is  
given in an arbitrary unit. In other words, comparison is  
possible among inventive examples alone or comparative  
15 examples alone measured under the same conditions.

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【0029】

【Table 1】

Mixture compositions of starting powders(unit:% by mass)

			<u>S i<sub>3</sub>N<sub>4</sub></u>	<u>L a<sub>2</sub>O<sub>3</sub></u>	<u>C e O<sub>2</sub></u>	<u>E u<sub>2</sub>O<sub>3</sub></u>
5	E x a m p l e	1	4 6 . 0 1	4 3 . 2 7	1 0 . 7 2	0
		2	4 5 . 5 9	4 2 . 8 7	0	0
		3	4 5 . 9	4 3 . 1 6	0	1 0 . 9 4
		4	4 6 . 2 6	5 3 . 1 7	0 . 5 7	0
		5	4 6 . 1 3	4 8 . 2 1	5 . 6 6	0
10		6	4 5 . 5 8	2 6 . 4 6	2 7 . 9 6	0
		7	4 5 . 1 8	1 0 . 4 9	4 4 . 3 3	0
		8	4 3 . 2 8	4 0 . 2	1 0 . 6 2	0
		9	3 7 . 8 1	4 5 . 1 5	1 1 . 9 3	0
		1 0	3 7 . 4 2	4 4 . 6 9	0	0

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【Table 1 (continued)】

		<u>T b<sub>4</sub>O<sub>7</sub></u>	<u>A l<sub>2</sub>O<sub>3</sub></u>	<u>A l N</u>	<u>L a N</u>	
20	E x a m p l e	1	0	0	0	
		2	1 1 . 5 4	0	0	
		3	0	0	0	
		4	0	0	0	
		5	0	0	0	
		6	0	0	0	
		7	0	0	0	
25		8	0	0	5 . 9	
		9	0	1 . 9 6	3 . 1 6	0
		1 0	1 2 . 8 2	1 . 9 4	3 . 1 2	0

【0030】

【Table 2】

Parameters for design compositions

		Parameters					
		a	b	c	d	e	f
5	Ex. 1	0.57	2.43	9	0	12	4.5
	Ex. 2	0.57	2.43	9	0	12	4.5
	Ex. 3	0.57	2.43	9	0	12	4.5
	Ex. 4	0.03	2.97	9	0	12	4.5
10	Ex. 5	0.3	2.7	9	0	12	4.5
	Ex. 6	1.5	1.5	9	0	12	4.5
	Ex. 7	2.4	0.6	9	0	12	4.5
	Ex. 8	0.533	2.467	8	0	11	4
	Ex. 9	0.6	2.4	7	1	10	5
15	Ex. 10	0.6	2.4	7	1	10	5

【0031】

Examples 2-10;

The starting powders used herein were the same silicon nitride powders, lanthanum oxide powders and cerium nitride powders as in Example 1 as well as europium oxide powders with a 99.9% purity, terbium oxide powders with a 99.9% purity, aluminum oxide powders with a 99.9% purity and lanthanum oxide powders with a 99.9% purity. Oxy nitride powders were prepared following Example 1 with the exception that the compositions set out in Tables 1 and 2 were used. As a consequence of X-ray diffractometry upon pulverization of the synthesized samples, the compositions in Examples 2 to 8 were all identified as the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  phase, and the compositions in Examples 9 and 10 were all identified as the  $\text{La}_3\text{Si}_{8-x}\text{Al}_x\text{N}_{11-x}\text{O}_{4+x}$  phase. Further, there were obtained fluorescent materials that

were excited by ultraviolet radiation to give out visible light with high luminance, as shown in Examples 2 to 10 in Table 3. In particular, the samples with Ce added thereto provided excellent blue fluorescent materials and the sample with Tb added thereto provided excellent green fluorescent materials.

【0032】

【Table 3】

Peaks, wavelengths and intensities of excitations and emission spectra under fluorometry

<u>Light Emission</u>					
	Wavelength	Intensity	Wavelength	Intensity	
	nm	AU*	nm	AU*	
Ex. 1	424	1239	371	1242	
Ex. 2	542	1124	256	1122	
Ex. 3	501	32	428	33	
Ex. 4	425	809	370	790	
Ex. 5	431	1421	372	1415	
Ex. 6	433	1720	372	1733	
Ex. 7	435	1056	374	1049	
Ex. 8	436	2013	372	2002	
Ex. 9	430	1884	365	1887	
Ex. 10	545	1911	258	1881	

AU\*: Arbitrary Unit

【POSSIBLE APPLICATIONS TO THE INDUSTRY】

【0033】

The present invention provides a novel oxynitride fluorescent material, which is capable of emitting light with higher luminance and is lesser likely to decrease in luminance and deteriorate as compared with conventional sialon, and so lends itself well to VFDs, FEDs, PDPs, CRTs,

white LEDs and so on. This fluorescent material will have wide applications to material designs in such fields.

【BRIEF DESCRIPTION OF THE DRAWINGS】

【0034】

5            Fig. 1 is a spectral diagram for excitation and emission spectra of one embodiment of the inventive oxynitride (Example 1).

            Fig. 2 is a spectral diagram for excitation and emission spectra of another embodiment of the inventive  
10 oxynitride (Example 2).

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